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(54) Thermosetting, thermally expanding molded articles

(57) Bonding agents that contain at least one liquid, reactive epoxy resin, possibly flexibility-enhancing agents and reagent thinners and at least one fine-sized thermoplastic polymer powder and hardener/accelerators and foaming agents, are suitable for the manufacture of thermosetting, thermally expanding molded articles by the injection-molding procedure. In preferred implementation forms the bonding agent is injected onto a metallic or thermoplastic support.

Description

[0001] The invention concerns thermosetting, thermally expanding molded articles that are not sticky at room temperature, a procedure for their manufacture, their use and a procedure to strengthen and/or reinforce vehicle body parts.

[0002] Metallic light-weight structural components for constant, accurately sized mass production, of a specified rigidity and structural strength are ever more frequently required. In particular in the motor vehicle area and as a consequence of the weight decrease desired, the demand for metallic light-weight structural parts made of thin-walled sheet metal that nevertheless are sufficiently rigid and have sufficient structural strength is increasing.

[0003] EP-A 0 798 062 proposes components of metallic foam, where the metallic foam is manufactured from a metal powder and a foaming agent and possibly formed between solid metallic sheets in a press, at high temperatures and high pressures. Such a procedure is suitable only for large-size components that are manufactured separately from the assembly line of motor vehicles and then incorporated into the normal assembly process. The insertion and foaming of metallic foams is not possible under the process conditions of a normal motor vehicle assembly line.

[0004] US-A 4,978,562 describes a specifically light reinforcing door pillar made of a composite material consisting of a metal tube filled in part with a specifically light polymer of cellular structure. It is proposed to mix in an extruder thermosetting resins based on epoxy resins, vinyl ester resins, unsaturated polyester resins and polyurethane resins with the corresponding hardeners, fillers and cell-forming agents, to harden this mixture to a core, inserting it in the metal tube in such a way that it is fixed in the tube by friction forces or mechanically. Alternatively the polymer core can be manufactured from liquid or pasty polymer material by casting and then pressed into the tube. No reactive, thermosetting and thermally expanding molded article is disclosed.

[0005] US-A 4,769,391 describes a preformed composite insert for insertion in a hollow structural body. This insert part contains numerous thermoplastic granulates of a mixture of a thermoplastic resin and not expanded expanding hollow micro-beads and a matrix of expanded polystyrene that contains the granulates mentioned. The thermoplastic resin of the granulates can be a thermoplastic – such as a thermoplastic polyester – or it can be a thermosetting epoxy resin. After inserting the part in the hollow body to be filled, the component is heated to a temperature that causes the "vaporization" of the expanded polystyrene. Here "vaporization" means the degradation of the expanded polystyrene to a thin film or carbon black. At the same time the thermoplastic granulate particles expand and possibly harden, where depending on the degree of expansion of the granulate, more or less large cavities remain between the individual expanded granulate particles.

[0006] Similarly US-A 4,861,097 and US-A 4,901,500 describe specifically light composite pillars of foamed polymers and metallic structures to reinforce motor vehicle doors. According to this theory the polymeric core is first formed by

manufacturing a liquid or pasty reinforcement material that is subsequently injected or cast into a channel-like structure and then hardened. This hardened core part is then introduced into the hollow metallic structure. Alternatively the core can be preformed or precast by injection molding and then placed in the cavity.

[0007] WO 89/08678 describes a procedure and compositions to reinforce structural elements, where the polymeric reinforcing material is a two-component epoxy system, in which one component is a dough-like mass based on epoxy resins and the second component is a mixture of fillers, a colored pigment and a liquid hardening agent of dough-like consistency. Immediately prior to filling the reinforcing material into the cavity, the two components are mixed, placed into the cavity structure and hardened, where the hollow structure may be preheated.

[0008] WO 96/37400 describes a W-shaped reinforcing configuration that contains a thermally expanding resin-like material, which is introduced into the hollow structure to be reinforced. The reinforcing polymeric matrix preferably consists of a single-component, dough-like system that includes an epoxy resin, an acrylonitrile-butadiene rubber, fillers, high-strength glass beads, a hardener and an accelerator, as well as a foaming agent based on an azo-compound or a hydrazide compound.

[0009] WO 98/15594 describes foamed products for use in the automobile industry, based on preferably liquid, two-component epoxy systems, in which one component consists of a liquid epoxy resin and metal carbonates or bicarbonates and the other component of pigments, possibly hollow beads and phosphoric acid. When these two components are mixed, the compositions harden with foaming. No applications to reinforce or strengthen hollow structures are disclosed.

[0010] The polymeric materials of the preceding state of the art are either not suitable for the manufacture of preformed molded parts that at a later time expand thermally upon heating and are hence thermosetting, or, if they are suitable for this purpose, as a rule have a very sticky surface that leads to contaminating the storage areas, and on the other hand, bond dirt and dust. In addition, a sticky surface on these molded articles impedes handling and in particular storage, as for instance the stacking of several articles on top of each other. For this reason molded articles of the state of the art are equipped with a protective foil that is removed immediately prior to their use. However, such protective foils make the manufacture and use of such molded articles more expensive; in addition, the protective foils have to be disposed of, once removed, which causes additional costs.

[0011] To reduce the surface stickiness of such molded articles WO 00/52086 proposes manufacturing thermosetting, thermally expanding molded articles from a mixture consisting of at least one solid reactive resin, at least one liquid reactive resin, at least one flexibility-enhancing reactive resin and hardeners and/or accelerators or foaming agents. These molded articles are suitable for strengthening and/or reinforcing thin-walled metal constructions and for strengthening hollow metallic light-weight constructions. Compared to known thermosetting, thermally expanding molded articles, the molded articles

according to the theory of this document are characterized by improved shape stability in the not-yet-hardened state and by low surface stickiness. The properties of processability and shape stability are achieved by mixing epoxy resins of different melting points. However, for instance the reduced surface stickiness can always be achieved only within a very narrow temperature interval, so that a formulation that is not sticky in winter can have a very sticky surface in summer. In addition, this procedure requires the use of large amounts of expensive resin and hardener systems. In particular, for the cost-effective manufacture of such expanding molded articles by injection molding, difficulties during production and handling keep arising; this is undesirable for the process certainty of the manufacturing procedure.

[0012] Against the background of this state of the art, the inventors posed the task of making available non-sticky molded articles to reinforce and/or strengthen metal sheets or metallic hollow bodies that

are thermosetting,
are thermally expanding,
and have good strengthening and/or reinforcing effects on thin-walled metallic structures,
can be cast in the injection molding procedure at several temperatures, preferably onto a support,
are dimensionally stable to 50°C, after injection molding,
can be transported without expensive packaging,
and can be manufactured cost-effectively and simply, both as a mass and as a molded article.

[0013] The solution according to the invention of this problem can be found in the patent claims.

[0014] It essentially consists in making available bonding agents for the manufacture of thermosetting, thermally expanding molded articles that contain

(a) at least one liquid reactive resin,
(b) possibly a flexibility-enhancing agent,
(c) possible a reagent thinner,
(d) at least one small-particle thermoplastic polymer powder,
(e) hardeners and/or accelerators,
(f) a foaming agent.

[0015] Preferably the thermally expanding molded articles are manufactured by injection molding at low pressures and low temperatures.

[0016] Another object of the present invention is a procedure to strengthen and/or reinforce vehicle body components, which involves the following essential operations.

[0017] In a first step, the bonding agent constituents mentioned earlier are homogeneously mixed at temperatures below 110°C and then transferred to an injection molding plant. This bonding agent is from there injected into an injection

molding mold at temperatures of 60-110°C, preferably of 70-90°C under controlled temperature conditions. A support of metal or thermoplastic materials is possibly placed in the mold, onto which the expanding bonding agent is injected. The molded article is then cooled to temperatures below 50°C; once released from the mold, the surface of the expanding bonding agent is non-tacky, so that the expanding molded articles can be packaged without any impediments and can survive long trips during the summer without problems, even in southern countries, without requiring reefer cars.

[0018] In a final application the expanding molded article is placed on the areal metallic substrate or in the cavity to be strengthened, for instance in a motor vehicle body, and fixed there. In the subsequent process heat of the baking ovens the temperature of the vehicle body is heated to temperatures of 110-200°C; during this heating process the volume of the molded article expands by 50-300% and the reactive resin matrix hardens to a duroplast.

[0019] A further object of the present invention is hence the use of the expanding molded article to strengthen and reinforce areal sheet metal parts and/or metallic hollow structures, in particular hollow parts of vehicle bodies, such as body frames, body members, body pillars and broader interstices and gaps between body parts in motor vehicle construction.

[0020] Below we shall describe the bonding agent system especially suitable for an injection molding procedure for the manufacture of thermosetting, thermally expanding molded articles.

[0021] Numerous poly-epoxides with at least two 1,2-epoxy groups per molecule are suitable as epoxy resins. The epoxide equivalent of these poly-epoxides can vary between 150 and 50,000, preferably between 170 and 5,000. In principle the poly-epoxides can be saturated, unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic poly-epoxide compounds. Some examples of suitable poly-epoxides include the poly-glycidyl ethers manufactured by reaction of epichlorohydrin or epibromohydrin with a poly-phenol in the presence of alkali. Some poly-phenols suitable for this purpose are for instance resorcinol, catechol, hydroquinone, bisphenol A (bis-(4-hydroxyphenyl)-2,2-propane)), bisphenol F (bis-(4-hydroxy-phenyl methane), bis-(4-hyrdoxyphenyl)-1,1-isobutane, 4,4'-dihydroxy-benzophenone, bis-(4-hydroxyphenyl)-1,1-ethane, 1,5-hydroxy-naphthalene. Other suitable poly-phenols as base for the poly-glycidyl ethers are the known condensation products of phenol and formaldehyde of the novolak resin type.

[0022] Other poly-epoxides are poly-glycidyl esters of poly-carboxylic acids, for instance reactions of glycidol or epichlorohydrin with aliphatic or aromatic poly-carboxylic acids such as oxalic acid, succinic acid, glutaric acid, terephthalic acid or dimeric fatty acids.

[0023] Other epoxides are derived from the epoxidation products of olefinically unsaturated cycloaliphatic compounds or of natural oils and fats.

[0024] Epoxy resins derived from reactions of bisphenol A or bisphenol F with epichlorohydrin are very especially preferred, where the liquid epoxy resins are preferably based on bisphenol A and have a sufficiently low molecular weight. As a rule, epoxy resins that are liquid at room temperature have an epoxide-

equivalent weight of 150-480, approximately; the epoxide-equivalent weight is especially preferred in the range of 182-350.

[0025] The flexibility-enhancing agents to be used can be epoxy resins with flexibility-enhancing effect, such as the *per se* known adducts of carboxyl-terminated butadiene-acrylonitrile copolymers (CTBN) and liquid epoxy resins based on diglycidyl ethers of bisphenol A. Some concrete examples are the reaction products of the Hycar CTBN 1300X8, 1300X13 or 1300X15 of the B.F. Goodrich company with liquid epoxy resins. It is furthermore possible to use the reaction products of amino-terminated poly-alkene glycols ("Jettamines") with an excess of liquid poly-epoxides. Such reaction products are for instance disclosed in WO 93/00381. In principle it is also possible according to the invention to use reaction products of mercapto-functional prepolymers or liquid Thiokol polymers with an excess of poly-epoxides as flexibility-enhancing epoxy resins. However, most especially preferred are the reaction products of polymeric fatty acids, in particular of dimeric fatty acids, with epichlorohydrin, glycidol or in particular, diglycidyl ethers of bisphenol A (DGBA). The copolymers of acrylonitrile with butadiene and/or isoprene and possibly (meth)acrylic acid with an acrylonitrile content of 10-50 wt.-%, preferably of 20-40 wt.-% and a (meth)acrylic acid content of 0.0-1 wt.-%, preferably of 0.0-0.1 wt.-% are also suitable as flexibility-enhancing agents. Mixtures of the flexibility-enhancing agents mentioned precedingly can also be used.

[0026] Another essential component of the bonding agent composition according to the invention are reagent thinners. Reactive thinners in the sense of this invention are epoxide group-containing, low-viscosity substances (glycidyl ethers or glycidyl esters) of aliphatic or aromatic structure. These reagent thinners serve on the one hand to lower the viscosity of the bonding agent system above the softening point and on the other, control the pregelling process during injection molding. Some typical examples of the reagent thinners to use according to the invention are mono, di or tri-glycidyl ethers of C_6-C_{14}-monohydric alcohols or alkyl-phenols and the monoglycidyl ethers of cashew nut shell oils, diglycidyl ethers of ethylene glycol, diethylene glycol, triethylene glycol, tetra-ethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, 1,5-pentanediol, 1,6-hexanediol, cyclohexane-dimethanol, triglycidyl ethers of trimethylol-propane and the glycidyl esters of C_6-C_{24}-carboxylic acids, or their mixtures.

[0027] Since the molded articles hardening according to the invention are of a single-component configuration and are thermosetting, they furthermore contain a latent hardener and/or in addition, one or several accelerators.

[0028] Among the thermally activated or latent hardeners for the epoxy bonding agent system of components a), b) and c). it is possible to use guanidines, substituted guanidines, substituted ureas, melamine resins, guanamine derivatives, cyclic tertiary amines, aromatic amines and/or their mixtures. Here the hardeners can either be included stoichiometrically in the hardening reaction, or also act as catalysts. Some examples of substituted guanidines are methyl-guanidine, dimethyl-guanidine, trimethyl-guanidine, tetramethyl-guanidine, methyl-iso-biguanidine, dimethyl-iso-biguanidine, tetramethyl-iso-biguanidine, hexamethyl-iso-biguanidine, heptamethyl-iso-biguanidine and most especially,

cyano-guanidine (dicyandiamide). Some representatives of suitable guanamine derivatives to mention are alkylated benzo-guanamine resins, benzo-guanamine resins or methoxymethyl-etoxymethyl-benzoguanamine. The criterion for a choice for single-component thermosetting bonding agents is naturally the low solubility of these materials in the resin system at room temperature, such that here solid, finely milled hardeners have the preference. Dicyandiamide is particularly suitable. This ensures good storage stability for the composition.

[0029] In addition to or instead of the precedingly mentioned hardeners it is possible to use catalytically active substituted ureas. They are in particular p-chlorophenyl-N,N-dimethyl-urea (Monuron), 3-phenyl-1,1-dimethyl-urea (Fenuron) or 3,4-dichlorophenyl-N,N-dimethyl-urea (Diuron). In principle it is also possible to use catalytically active tertiary acryl or alkyl-amines, such as benzyl-dimethyl-amine, tris-(dimethylamino)-phenol, piperidine or piperidine derivatives, but they often have too high a solubility in the bonding agent system, so that here no useful storage stability of the single-component system is attained. In addition, various preferably solid imidazole derivatives can be used as catalytically acting accelerators. Some representatives are 2-ethyl-2-methyl-imidazole, N-butyl-imidazole, benz-imidazole and N-C_1-C_{12}-alkyl-imidazoles, or N-aryl-imidazoles, triazine derivatives and imidazole/triazine compounds (for instance C_{11}-Z-azines). It is also possible to use combinations of hardeners and accelerators in the form of so-called accelerated dicyandiamides in finely milled form.

[0030] This occasionally rendered superfluous the separate addition of catalytically active accelerators to the epoxide-hardening system.

[0031] In the case of particularly reactive systems it is also possible to use finely milled powdery hardening accelerators based on adducts of amines to epoxy resins; these adducts have tertiary amine groups and epoxy groups. The latent powdery accelerators can be used in combination with the latent hardeners and/or accelerators previously mentioned.

[0032] The bonding agents according to the invention furthermore contain at least one fine-particle thermoplastic polymer powder. These thermoplastic polymer powders can in principle be chosen from among numerous fine-particle polymer powders; as an example we shall mention vinyl acetate homopolymer, vinyl acetate copolymers, ethylene-vinyl acetate copolymers, vinyl chloride homopolymer (PVC), or copolymers of vinyl chloride with vinyl acetate and/or (meth)acrylates, styrene homo or copolymers, (meth)acrylate homo or copolymers, or polyvinyl butyral. The especially preferred thermoplastic polymers contain functional groups such as carboxyl groups, carboxylic acid anhydride groups, or imidazole groups and have a core/shell structure, where the shell of these polymers shows only a small swelling behavior at room temperature, with respect to softeners or reagent thinners. However, during the pregelling reaction in injection molding, these core/shell polymers swell quite rapidly and immediately cause a very sticky surface on the expanding bonding agent layer, after the injection-molding formed piece cools. Such core/shell polymers are for instance described in EP 30 999 A1, EP 30590 A1, DE 27 22 752 A1, or US 5,290,857. These polymer powders should have a mean particle size below 1 mm, preferably below 350 µm and especially preferred, below 100 µm.

[0033] As a rule the bonding agents according to the invention in addition contain *per se* known fillers, such as the diverse milled or precipitated chalks, carbon black, calcium-magnesium carbonates, barite and in particular, siliceous fillers of the aluminum-magnesium-calcium silicate type, for instance wollastonite, chlorite, etc.

[0034] It is a goal according to the invention to use the thermally expanding, thermosetting molded articles for the manufacture of specifically light structures. For this reason, in addition to the " normal" fillers just mentioned, they contain so-called light fillers, chose from the groups of hollow metal beads – such as hollow steel beads, hollow glass beads, fly ash [Fillites], hollow plastic beads based on phenolic resins, epoxy resins or polyester, expanded hollow micro-beads with wall materials of (meth)acrylic acid ester copolymerides, polystyrene, styrene-(meth)acrylate copolymers and in particular, of poly-vinylidene chloride, as well as copolymers of vinylidene chloride with acrylonitrile and/or (meth)acrylic acid esters, hollow ceramic beads; or organic light fillers of natural origin, such as milled nutshells, for instance the shells of cashew nuts, coconuts or peanut shells and cork meal or coke powder. Especially preferred are those light fillers based on hollow micro-beads that ensure high pressure resistance of the molded article in the hardened molded article matrix.

[0035] In a specially preferred implementation form the matrix materials for the thermosetting, thermally expanding molded article contain, in addition, fibers based on aramide fibers, carbon fibers, metal fibers – for instance of aluminum - glass fibers, polyamide fibers, polyethylene fibers or polyester fibers, where these fibers are preferably pulp fibers or staple fibers, with a fiber length of 0.5-6 mm and a diameter of 5-20 µm. Here polyamide fiber of the aramide-type fibers are especially preferred, or also polyester fibers.

[0036] While in principle the known foaming agents are suitable, for instance the "chemical foaming agents" that release gases during their decomposition, or "physical foaming agents", i.e. expanding hollow beads. Some examples of the first type of foaming agent are azo-bis-isobutyro-nitrile, azo-dicarbonamide, di-nitroso-pentamethylene-tetramine, 4,4'-oxy-bis-(benzenesulfonic acid hydrazide), diphenylsulfone-3,3'-disulfo-hydrazide, benzene-1,3-disulfo-hydrazide, p-toluene-sulfonyl-semicarbazide. However, the expanding plastic hollow micro-beads based on polyvinylidene chloride copolymers are especially preferred, or acrylonitrile/(meth)acrylate copolymers, which are commercially available under the names "Dualite" or "Expancel" from the Pierce & Stevens or the Casco Nobel companies, respectively.

[0037] The adhesive compositions according to the invention may additionally contain common adjuvants and additives, such as softeners, reactive thinners, rheology aids, wetting agents, adhesion promoters, aging-protection agents, stabilizers and/or colored pigments. Depending on the requirement profile for the molded article in terms of its processing properties, flexibility, demanded strengthening effect and the adhesive bond to the substrates, the mass ratios of the individual components can vary within relatively wide margins. Typical ranges for the essential components are:

(a) thermoplastic polymer powder	5-50 wt.-%, preferably 15-25 wt.-%,
(b) liquid epoxy resins	10-50 wt.-%, preferably 30-40 wt.-%,
(c) flexibility-enhancing agents	1-25 wt.-%, preferably 5-15 wt.-%,
(d) reagent thinners	1-15 wt.-%, preferably 1-10 wt.-%,
(e) hardeners and accelerators	1.5-5 wt.-%,
(f) foaming agents	0.5-5 wt.-%,
(g) light fillers	20-40 wt.-%,
(h) fillers	5-20 wt.-%,
(i) fibers	0.1-30 wt.-%, preferably 0.5-20 wt.-%,
(j) pigments	0-1 wt.-%.

where the sum of all constituents is 100 wt.-%

[0038] For the manufacture of the bonding agents according to the invention, the epoxy resin(s), flexibility-enhancing agents, reagent thinners and thermoplastic polymer are homogenized together with the fillers, fibers and pigments in a customary mixing aggregate such as a double-motion mixer, kneader or similar device; next the foaming agent and the hardener and accelerator are mixed in and here the temperature of the material must not exceed 110°C, but preferably not exceed 60-90°C, in particular during and after the addition of foaming agents and hardeners and/or accelerators.

[0039] The bonding agent thus manufactured can go into intermediate storage or be sent directly to the transport device of an injection molding machine. To manufacture the expanding molded article, as a rule next a support is placed in the mold. This support may be of metal, for instance a galvanized steel sheet, aluminum or also a thermoplastic material such as polyamide (PA), polyphenylene sulfide (PPS), polyphenylene ether (PPE), polyphenylene sulfone (PPSU), or polyphenyleme imide (PPI). Possibly these supports of thermoplastic materials can be reinforced with fibers; however, they must be characterized by low water incorporation and dimensional stability to up to 180°C.

[0040] After closing the mold the bonding agent, heated to temperatures of 60-110°C, preferably 70-90°C is injected into the mold; the molded article is then cooled, followed by the removal of the molded article. At the temperatures mentioned above the bonding agent is of low viscosity and can hence be readily transported through pumps and presses at low pressures. The molded articles obtained after cooling are dimensionally stable and not sticky to at least 50°C and need no specially manufactured shape-supporting packaging for storage. For this reason the molded articles can be transported to the end user, even in summer, over long distances in southern lands, without using reefer cars or refrigerated containers. At the end user the molded articles, depending on the application, are either placed inside the cavity to be strengthened or reinforced, or possibly, the molded articles can be installed already in the bare structure, in such a way that during the subsequent fitting processes the cavity if formed only by fitting other body parts. In addition, the molded articles according to the invention can be applied to areal sheet metal parts, for instance wide joints and/or gaps in vehicle body parts. As a rule the molded articles are dimensioned in such a way that they don't completely fill the cavities or joints and gaps in the

unexpanded state, so that subsequent process liquids – such as wash and cleaning baths, phosphatizing and converting baths as well as electro dip paints - are able to fully wet the metallic substrate surface. Occasionally the manufacturing lines include so-called "bare structure ovens", with temperatures of up to 140°C, to pregel adhesive and sealing materials. In these cases the molded articles according to the invention should not yet expand and harden in the bare structure ovens. Only in the following ovens for the hardening of the electro dip paint, at temperatures of 110-200°C, preferably at 140-180°C, will the expansion of the molded articles by 50-100% take place; at the same time the reactive resin matrix of the bonding agent system hardens to a duroplast, which then fills the cavities in such a way that a strengthening and reinforcing effect can occur.

[0041] In the hardened and foamed state the molded article matrix has a compressive strength of 6-30 MPa and a pressure modulus of 300-1500 MPa and thereby accomplishes a high reinforcing and strengthening effect at a low specific weight.

[0042] A preferred application of expanding molded articles is the strengthening and reinforcement of sheet metal parts and/or metallic hollow structures, in particular vehicular body frames, body members and the A, B and/or C pillars or hollow spaces of doors in automobile construction.

[0043] In the implementation examples below the invention is further elucidated; here the selection of examples is not intended to limit the scope of the object of the invention: they merely model individual implementation forms and advantageous effects of the invention.

[0044] All amounts specified in the examples below are fractions by weight or wt.-%, unless otherwise indicated.

Examples

[0045] The bonding agent compositions listed in the Table below were mixed to homogeneity in a double-action mixer, ensuring that the temperature did not go beyond the 50°C mark.

Table

	1	2	3	4	5	6
Epoxy resin, liquid 1)	55	55	55	55	-	55
Glycidyl ether 2)	-	-	5	-	10	-
Epoxy resin, solid 3)	-	-	-	-	55	-
Core-shell acrylate 4)	25	-	-	-	-	-
Polyacrylate 5)	-	25	-	-	-	-
Polyacrylate 6)	-	-	25	25	15	0
Hollow micro-beads 7)	2	2	2	2	2	2
Dicyandiamide	3	3	4	4	4	4
Amine adduct 8)	1.5	0.8	1	1	1	1

Calcium carbonate [9]	-	4.3	-	3	3	3
Glass fibers [10]	-	-	-	-	-	20
Hollow glass beads [11]	13.5	10	9	10	-	-
Gelling temperature, °C	-	102	84	-	-	-
Gelling time (at 100°C), sec	-	-	8	-	-	-
Density, gelled, g/cm	-	0.987	0.957	-	-	
Density, hardened, g/cm	-	0.509	0.612	-	-	-
Foaming degree	-	94	57	-	-	-
Compressive strength. N/mm^2	23.6	12.8	17.7	-	-	-
Tensile & share resistance, N/mm^2	-	3.9	3.2	-	-	-

Remarks

[1] liquid epoxy based on DGBA, epoxide equivalent 250
[2] monoglycidyl ether of a C_{12}/C_{14}-alcohol, epoxide equivalent 314
[3] solid epoxy, molecular weight approximately 880, melting range 50-62°C; epoxide equiv. 475
[4] according to the theory of US 5,290,857
[5] powdery poly(methyl methacrylate), Tg 124°C
[6] MMA/butyl methacrylate copolymer
[7] foaming agent (hollow plastic beads "Expancel DU 140", Pierce & Stevens company)
[8] finely milled accelerator (amine adduct on epoxy resin with epoxy- and tertiary amine groups
[9] precipitated
[10] short fibers, 17 µm fiber diameter, 3 mm long
[11] hollow glass micro-beads (Scotchlite VS 5500, compressive strength approx. 38 MPa, 3M company

[0046] To simulate injection molding, the compositions were each pregelled at 110°C for 5 min, which corresponds to pregelling in the injection molding mold of the injection molding machine. After pregelling the test specimens were dimensionally stable and had a non-sticky surface. To determine the degree of foaming, the density in the hardened state, the compressive strength of the molded article and the shearing strength, the briquettes were baked for 38 min at 150°C. As can be seen from the test results in the table above, good degrees of foaming, excellent compressive strength and combined tensile and shearing resistance were achieved with the briquettes according to the invention. Hence these materials are outstandingly suited to strengthen and reinforce hollow structures in the motor vehicle area.

Patent claims

1. Bonding agents for the manufacture of thermosetting, thermally expanding molded articles that contain

(a) at least one liquid reactive epoxy resin,
(b) possibly a flexibility-enhancing agent,
(c) possibly a reagent thinner,
(d) at least one small-particle thermoplastic polymer powder,

(e) hardeners and/or accelerators,
(f) a foaming agent.

2. Bonding agents according to claim 1, **characterized by** the liquid epoxy resin (a) having a molecular weight greater than 350, preferably greater than 450.

3. Bonding agents according to claims 1 through 2, **characterized by** the flexibility-enhancing agent being chosen from rubber-modified epoxy resins, polyurethane-modified epoxy resins, adducts of amino-terminated poly-oxyalkenes and poly-epoxides, adducts of dimeric fatty acids and bisphenol A-diglycidyl ethers, adducts of polyether-polyols and epoxy resins, polysulfide- or polymercaptan-modified epoxy resins, copolymers of acrylonitrile and butadiene and/or isoprene and possibly (meth)acrylic acid, with an acrylonitrile content of 10-50 wt.-%, preferably of 20-40 wt.-% and a (meth)acrylic acid content of 0.0-1 wt.-%, preferably of 0.0-0.1 wt.-%, or mixtures of the flexibility-enhancing agents mentioned precedingly.

4. Bonding agents according to claims 1 through 3, **characterized by** the reagent thinner being chosen from mono, di or triglycidyl ethers of C_6-C_{14}-monohydric alcohols, alkyl-phenols, monoglycidyl ethers of cashew nutshell oils, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, 1,5-pentanediol, 1,6-hexanediol, cyclohexane-dimethanol, trimethylol-propane, glycidyl esters of C_6-C_{24}-carboxylic acids, or their mixtures.

5. Bonding agents according to at least one of the preceding claims, **characterized by** the hardener used being dicyandiamide in amounts of up to 5 wt.-% relative to the total composition, and possibly one or more accelerators.

6. Bonding agents according to at least one of the preceding claims, **characterized by** the thermoplastic polymer powder being a vinyl acetate homo or copolymer, an ethylene-vinyl acetate copolymer, a vinyl chloride homo or copolymer, a styrene homo or copolymer, a (meth)acrylate homo or copolymer, or a polyvinyl-butyral, or a mixture of two or more of these polymers, with a mean particle size of below 1 mm, preferably below 350 μm and very especially preferred, of below 100 μm.

7. Bonding agents according to at least one of the preceding claims, **characterized by** in addition containing fillers, where at least part of the fillers are light fillers, chosen from hollow metal beads, hollow glass beads, Fillite (fly ash), plastic hollow beads based on phenolic resins, epoxy resins, polyesters or hollow micro-beads with a wall material of (meth)acrylic acid ester copolymers, polystyrene, styrene-(meth)acrylate copolymers and in particular, of polyvinylidene chloride and copolymers of vinylidene chloride with acrylonitrile and/or (meth)acrylic acid esters, ceramic hollow beads or organic light fillers of natural origin, such as milled nutshells, cork meal or coke powder.

8. Bonding agents according to at least one of the preceding claims, **characterized by** the foaming agent (f) being expanding hollow micro-beads.

9. Bonding agents according to at least one of the preceding claims, **characterized by** containing fibers based on aramide fibers, carbon fibers, metal fibers, glass fibers, polyamide fibers, polyethylene fibers or polyester fibers.

10. Bonding agents according to at least one of the claims 1 through 9, containing

(a) thermoplastic polymer powder	5-50 wt.-%, preferably 15-25 wt.-%,
(b) liquid epoxy resin	10-50 wt.-%, preferably 30-40 wt.-%,
(c) flexibility-enhancing agent	1-25 wt.-%, preferably 5-15 wt.-%,
(d) reagent thinner	1-15 wt.-%, preferably 1-10 wt.-%,
(e) hardeners and accelerators	1.5-5 wt.-%,
(f) foaming agents	0.5-5 wt.-%,
(g) light filler	20-40 wt.-%,
(h) fillers	5-20 wt.-%,
(i) fibers	0.1-30 wt.-%, preferably 0.5-20 wt.-%,
(j) pigments	0-1 wt.-%.

where the sum of all constituents is 100 wt.-%

11. Procedure to strengthen and/or reinforce vehicle body components, **characterized by** the following essential operations

a) mixing the bonding agent constituents according to at least one of the claims 1 through 10 at temperatures below 110°C, preferably below 50°C,

b) injection-molding the bonding agent at temperatures of 60-110°C, preferably at 70-90°C, possibly onto a support,

c) cooling the molded article,

d) fixing the molded article on the areal metallic substrate, or introducing it into the cavity to be strengthened, possibly with heating to the softening point of the molded article,

e) heating to temperatures of 110-200°C, preferably of 130-180°C, whereby the volume of the molded article expands by 50-100% and the reactive resin matrix hardens to a duroplast.

12. Injection-molded molded article according to claim 11, **characterized by** not being sticky at room temperature, following step e).

13. Injection-molded molded article according to claim 11a) through e) or 12, **characterized by** the support being of galvanized steel sheet, aluminum or of a thermoplastic material such as polyamide (PA), polyphenylene sulfice (PPS), polyphenylene ether (PPE), polyphenylene sulfone (PPSU), or polyphenylene imide (PPI).

14. Injection-molded molded article according to claim 13, **characterized by** the thermoplastic material being reinforced with fibers.

15. Utilization of the molded article according to one of the preceding claims 11(a) through (e) or 12 through 14 to strengthen and reinforce areal sheet metal parts and/or hollow metallic structures, in particular of hollow vehicle body parts such as body frames, members and pillars in automobile construction.

16. Motor vehicle or metallic component, **characterized by** being strengthened or reinforced by a procedure according to claim 11.

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